特集 —— 地球深部における化学的不均質 ——

High-Pressure and High-Temperature Carbon Isotope Fractionation in the Fe-C System: Implications for Carbon Dynamics in the Deep Earth

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Carbon, the fourth most abundant element in the solar system, is believed to be an important light element constituent in the Earth's core. The high carbon content of carbonaceous chondrites (3.2 wt.%) compared to bulk earth estimates, the presence of graphite/diamond and metal carbides in Iron meteorites, the high solubility of carbon into iron melts in the Fe-C system, all suggests the plausible presence of carbon in the Earth's core. However, the distribution of carbon isotopes in the core and deep mantle remains elusive. Newly reported experimental data and theoretical estimates on equilibrium carbon isotope fractionation between graphite/diamond and carbide phases suggests that iron carbide melt will preferentially gather ^{12}C than ^{13}C . These results are consistent with the carbon isotope distribution between graphite and cohenite (Fe_3C) observed in iron meteorites. The temperature dependent fractionation of carbon isotopes between carbide phases and elemental carbon can be an effective mechanism that might have created a ^{12}C -enriched core. If the Earth's core is a large reservoir of ^{12}C -enriched carbon, then it can result in large perturbations in surface carbon cycle caused by the flux of isotopically lighter carbon from the core-mantle boundary.

[carbon isotopes, earth's core, iron carbide, isotope fractionation]

1. Introduction

The distribution of carbon and its isotopic ratio in the deep Earth are poorly understood, mainly because of the uncertainties in the form of occurrence and its content in the core [1]. Being a candidate for the light element in the Earth's core, carbon is widely considered to have chemically partitioned to the metallic liquid during the accretion and differentiation of the Earth in a magma ocean environment [1–6]. The form in which carbon is dissolved in the Earth's core and its transport at the core-mantle boundary is of great importance for understanding the whole Earth carbon distribution as well as long-term carbon cycle [7–9].

Carbon isotopic composition has served as an extremely important proxy for constraining the terrestrial carbon cycle, because its isotopes fractionate extensively in low-temperature surface and

subsurface processes. Carbon has two stable isotopes of ^{12}C and ^{13}C . The difference in the isotopic ratio of $^{13}\text{C}/^{12}\text{C}$ in naturally occurring materials with that of global standard (Belemnite fossil in the Pee Dee Formation) is used for expressing the carbon isotopic composition. Carbon isotope ratio is expressed traditionally using the delta notation (δ), which is defined as.

$$\delta^{13}\text{C} \text{ (in } \text{‰}) = \frac{\left\{ \frac{^{13}\text{C}}{^{12}\text{C}} \right\}_{\text{Sample}} - \left\{ \frac{^{13}\text{C}}{^{12}\text{C}} \right\}_{\text{Standard}}}{\left\{ \frac{^{13}\text{C}}{^{12}\text{C}} \right\}_{\text{Standard}}} \times 1000 \quad (1)$$

and expressed in per mil (‰, parts per thousand)

Surface processes in the Earth are well known for fractionation of carbon isotopes between different reservoirs. For example, photosynthetic process of

carbon fixation produces a large carbon isotope fractionation that results in a preferential accumulation of ^{12}C in cellulose and therefore the biogenic materials generally have a lower $\delta^{13}\text{C}$ values than the CO_2 in the atmosphere.

In general, the carbon isotopic composition of upper mantle is considered as the carbon isotopic composition of the “bulk Earth” ($\delta^{13}\text{C} = -5 \pm 3\text{‰}$) [10,11]. Despite this consensus, there are several recent findings of isotopically light carbon, especially in diamonds derived from deep mantle sources [12,13]. Such observations are traditionally interpreted as evidence for the presence of recycled “biogenic” surface carbon brought down to the lower mantle by subduction-related processes [12,13]. Thus far, the heterogeneities in carbon isotopic composition in the upper mantle have been explained mainly by recycling process. However, recent studies have suggested the possible presence of ^{12}C enriched carbon in the core by fractionation processes during early accretion and segregation of metallic core [14,15]. Studies on other planetary materials in the solar system, such as howardite-eucrite-diogenite (HED) meteorites, shergottite-nakhlite-chassignite (SNC) meteorites and chondrites suggest that there is a remarkable difference in isotopic composition between these bodies and bulk silicate Earth values, the later being heavier than the former in the order of about 10 to 15‰ [16–18]. Thus, the validity of the assumption that the bulk Earth carbon isotope composition is equivalent to the carbon isotopic composition of silicate mantle is being debated recently [1,14,15]. It is therefore essential to clearly understand how far the fractionation of carbon isotopes has occurred during the segregation of core, what is going on in the present day at the core-mantle boundary and whether the carbon in the core has an impact on Earth’s carbon cycle and surface processes.

Previous studies on theoretical computations on equilibrium isotope fractionation using reduced partition function ratios derived from phonon spectrum between two carbon-bearing phases predict that the values converge at high-temperature conditions that are prevailing in mantle and core of the Earth [19] and hence not much attention has been paid to the

fractionation processes at high temperature conditions. However, our recent studies have suggested the possibility of large scale carbon isotopic fractionation even at temperatures in the order $>2000^\circ\text{C}$. Therefore, accretion, differentiation and segregation of metallic core in a magma ocean environment might have produced a remarkable carbon isotopic variation in the Early Earth [1,14,15], which we believe to have ultimately played a role in the mantle carbon isotopic heterogeneities of the present day Earth. In this article, we review the recent progress in the understanding of carbon isotope fractionation between different carbon-bearing phases potentially present in the deep Earth and explore the possibility of addressing the Earth’s long-term carbon cycling involving the core as a major stagnant reservoir that perturbs once in a while with plumes evolving from core-mantle boundary.

2. Carbon isotope fractionation at high-pressure and high-temperatures conditions

The carbon isotope fractionation between elemental carbon (graphite/diamond) and iron carbide melt were estimated in a pioneering study reported in Satish-Kumar *et al.* [14]. We estimated the temperature dependence from high-pressure high-temperature (HPHT) experiments in the Fe-C system at 5 GPa and 10 GPa under varying temperature conditions using a Kawai-type multi-anvil high-pressure apparatus. Graphite powder of known carbon isotopic composition ($\delta^{13}\text{C} = -24.4\text{‰}$) was mixed with Fe powder as the starting material for all experimental runs. The product phases were characterized using X-ray diffraction, field emission scanning electron microscopic observations and quantitative measurements of Fe and C contents using an electron microprobe.

The textural features and carbon elemental distribution maps of representative run products indicate that at 5 GPa and temperatures above 1500°C the mixture has completely melted and pristine graphite has crystallized suggesting the attainment of chemical and isotopic equilibrium (Fig. 1a,b). However, at lower temperatures, graphite forms globular ag-

gregates in a granular cementite matrix. This observation is consistent with the earlier experimental results showing peritectic melting relations at 1275°C and 2 GPa [20,21]. Recrystallization, coarsening and formation of euhedral graphite is clearly observed in all experimental runs above 1500°C (Fig. 1c,d). Diamond was the product phase at 10 GPa and 2100°C. At 5 GPa and in the temperature range from 1300°C to 1800°C, the solubility of carbon in the iron melt was between 6.4 and 6.8 wt.%. The solubility increased to about 7.5 wt.% at around 2000°C at 5 GPa, whereas at the diamond stability field of 2100°C and 10 GPa it was about 8.6 wt.%. The experimental results are more or less consistent, with earlier studies on phase relations in the Fe-C system [20,21]. Gravity separation of graphite from iron carbide melt was observed in some of the runs at high-temperatures and longer run durations. Diamond crystals were completely concentrated in the edge of the capsule.

The key point for the estimation of isotope fractionation is the precise and accurate measurement of iso-

topes of the phases concerned. In the case of Fe-C system, graphite/diamond could be separated to pure phases by acid digestion. However there is always a possibility that iron carbide-rich domain may contain some graphite/diamond inclusions that results in additional uncertainty. Carbon isotopic composition of separated phases of iron carbide and graphite/diamond could be precisely measured using a conventional gas source isotope ratio mass spectrometer (IRMS). Run products were mechanically and/or chemically separated to iron carbide melt fraction and graphite/diamond fraction for carbon isotope measurements. Mechanical separation includes manual dissection of run products under a binocular microscope using a dental drill. Separation of graphite from other materials was carried out using floatation method, because graphite usually has a high surface tension and floats in water. Chemical separation involved selective digestion of phases with different acids. For example carbonate dissolves in HCl, whereas silicates, oxides and carbides in HF, however graphite and diamond does not dissolve in both these acids. These methods were used for separating each phase as pure as possible for isotope analysis (see methods in Ref. [14] for more details). The results, plotted in a temperature-isotope fractionation diagram (Fig. 2), show the presence of distinct fractionation between graphite/diamond and iron carbide melt, where lighter carbon isotope fractionate to the iron carbide relative to graphite/diamond. A quantitative estimation of the carbon isotope fractionation between iron carbide and graphite/diamond (gr/dia) was made for the first time in that study which was supported by several later studies at varying temperature and pressure conditions [22–25].

Carbon isotope fractionation between graphite and cohenite has been reported from iron meteorites, where a fractionation of 11.5‰ and 12.5‰ for Canyon Diablo and Magura meteorites, respectively [26]. The crystallization of cohenite in Canyon Diablo cohenite formed at around 650°C and in Magura it was around 600°C [27]. The fractionation observed in these two meteorites fit well with our experimentally determined isotope fractionation between elemental carbon and iron carbide melt (Fig. 3). Therefore, the

Fig. 1. (Color online) Representative element distribution maps of run products of experiments in the Fe-C system. (a,b) Carbon and iron elemental distribution map of experimental run product at 1300°C and 5 GPa showing irregular carbon and iron distribution. (c,d) Carbon and iron elemental distribution map of experimental run product at 1600°C and 5 GPa showing their uniform distribution in iron carbide phase, proving the equilibrium distribution of carbon in the melt. Euhedral graphite crystal formed in the experimental runs above 1500°C.

Fig. 2. (Color online) Carbon isotope distribution between graphite/diamond and iron carbide phases. The phase relations observed in our run products relating to the temperature conditions of experimental runs are given in the top. Some of the analyses have mixed phases and the carbon isotopic composition fall between the data for pure phases. The analytical uncertainties are less than 0.1‰ for all measurements (after Ref. [14]).

Fig. 3. Equilibrium fractionation of carbon isotopes between graphite/diamond and Fe-C melt as a function of temperature (modified after Ref. [14]). For comparison the theoretical computation of fractionation between diamond and iron carbide is also shown (after Ref. [15]). The vertical line represent a possible temperature of crystallization of iron melt, which will correspond to a fractionation of 2‰.

temperature dependence of carbon isotope fractionation between iron carbide and elemental carbon also finds application in determining the temperature of formation of planetary bodies as well.

Together, the temperature dependence of carbon isotope fractionation was expressed as

$$\Delta^{13}\text{C}_{(\text{gr/dia} - \text{iron carbide melt})} = 8.85 \{10^6/T^2(\text{K})\} + 0.99 \quad (2)$$

In a recent study, Horita and Polyakov [14] have theoretically estimated the reduced partition function ratios (β factors) for carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) in Fe_3C using partial vibrational densities of states (PVDOSs) and observed that it is lowest for iron carbide phase among all possible carbon phases that may exist in the mantle. The ^{13}C β factors are similar to those estimated using density functional theory calculations for Fe_3C [28]. Together with the previously available experimental data, Horita and Polyakov was able to demonstrate that the ^{13}C is depleted in various carbides and carbon dissolved in Fe-Ni alloys at mantle conditions. Especially, at high temperatures the experimental determination of isotope fractionation seems to match very well with the theoretical estimates (Fig. 3).

3. Implications for carbon dynamics in the deep Earth

Models on Earth's core formation suggest that liquid metallic iron has immiscibly separated from the silicate magma ocean to form metal diapirs that descended to form the core [29,30]. It is likely that

these metallic melt diapirs have chemically and isotopically fractionated with the mantle materials. In such a scenario, our results on carbon suggest that the light ^{12}C will preferentially select iron melt than other carbon forms, whereas the heavy ^{13}C will remain in the mantle. If we consider that the differentiation of iron melt in a magma ocean environment has occurred at a temperature at around 2500°C , then the carbon isotope fractionation between iron carbide melt and carbon should be around 2.0‰ (Fig. 3).

The discovery of carbon isotope fractionation between iron carbide melt and graphite/diamond at high-temperature high-pressure conditions has important implications, especially during the early differentiation and formation of the Earth's core [14,15]. Our finding of the possible light carbon isotope-bearing core should imply that the bulk silicate Earth $\delta^{13}\text{C}$ value of around -5‰ may not be representative of the bulk Earth.

Wood *et al.* [1] discussed the plausible mechanisms for the formation of bulk silicate Earth carbon isotope value of -5‰ . Using a simple modelling of continuous core extraction with Rayleigh fractionation from a parent bulk isotopic composition of -20‰ , it was concluded that the modification of carbon isotopes in the Earth can be achieved, given that the uncertainties on formation temperatures and fractionation factors are considered. They have finally concluded that carbon isotopic composition of the bulk silicate Earth is consistent with Earth's core containing about 1 wt% of carbon. This conclusion is depending upon the assumption that the isotopic fractionation factors are accurate and the process of carbon extraction involves Rayleigh fractionation.

Horita *et al.* [15] further evaluated the fractionation of carbon isotopes between possible carbon-bearing phases using theoretical calculations and concluded that the temperature dependence of fractionation determined in the experimental studies generally agree with the theoretical estimates. They suggest that the formation of low $\delta^{13}\text{C}$ diamonds in mantle conditions have to consider the abiotic processes of fractionation between carbide phases and diamond at mantle conditions. They further suggest that the abiogenic process of carbon isotope fractionation in the deep

Earth might have implications on the evidences of early Earth's biogenic activity as carbon isotopic composition solely cannot be a convincing evidence in early Archean and Hadean times.

The study by Hayden and Watson [8] has proposed that the grain boundary diffusion of carbon in the core-mantle boundary (CMB) is a plausible mechanism for transport of carbon from Earth's core to mantle. If this process is the major mode of transport of carbon in the deep Earth, then the finding of ^{12}C -enriched core has further important implications in the deep carbon cycle of the Earth. Diffusion of ^{12}C is faster than ^{13}C and therefore the carbon at CMB should have further enriched in ^{12}C [8]. It is plausible that such isotopically light carbon from the CMB can be incorporated into the upwelling deep mantle plumes, which result in episodic large-scale volcanism in the Earth's surface [12]. A consequence of such "isotopically light carbon flux from the core" should be found as negative carbon isotopic perturbations in the Earth's geological history. The global negative carbon isotope excursions recorded in the Earth's history, such as those reported in the late Pliocene [31], has any direct relation to the isotopically light carbon flux from the Earth's core has to be tested in the future.

Stable isotope fractionation processes and the signatures they leave in deep Earth might be an important proxy for understanding the hidden light elements reservoirs. Recent studies have found that not only the light elements but also the major element stable isotopes fractionate at high temperature conditions [32–35]. The application of stable isotope geochemistry at high-temperature and high-pressure conditions in understanding the composition of deep Earth and other planetary bodies is yet to be explored. It is also important that the effect of pressure on stable isotope fractionation, which is negligible at crustal conditions, can also be a factor in understanding the deep Earth processes and has to be examined in the future [36]. Innovations in high-pressure experimental techniques together with advancements in accurate measurement of isotopic composition for small volume samples will together pave the way for our understanding of geochemical realms in the deep

Earth and will perhaps lead to new insights to our knowledge on planetary evolution.

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References

- [1] B.J. Wood, J. Li, A. Shahar: *Rev. Mineral. Geochem.*, **75**, 231 (2013).
- [2] B.J. Wood: *Earth Planet. Sci. Lett.*, **117**, 593 (1993).
- [3] T.N. Tingle: *Chem. Geol.*, **147**, 3 (1998).
- [4] B.J. Wood, M. Walter, J. Wade: *Nature*, **441**, 825 (2006).
- [5] R. Dasgupta, D. Walker: *Geochim. Cosmochim. Acta*, **72**, 4627–4641 (2009).
- [6] W.F. McDonough: In the *Mantle and Core* (ed. R.W. Carlson) Elsevier-Pergamon, Oxford (2003).
- [7] L.A. Hayden, B. Watson: *Nature*, **450**, 709–711 (2007).
- [8] L.A. Hayden, B. Watson: *Proc. National Acad. Sci.*, **105**, 8537 (2008).
- [9] J. Zachos, M. Pagani, L. Sloan, E. Thomas, K. Billups: *Science*, **292**, 686 (2001).
- [10] P. Deines: *Earth Sci. Rev.*, **58**, 247 (2002).
- [11] P. Cartigny, M. Palot, E. Thomassot, J.W. Harris: *Annu. Rev. Earth Planet. Sci.*, **42**, 699 (2014).
- [12] T.H. Torsvik, K. Burke, B. Steinberger, S.J. Webb, L.D. Ashwal: *Nature*, **466**, 352 (2010).
- [13] M.J. Walter, S.C. Kohn, D. Araujo, G.P. Bulanova, C.B. Smith, E. Gaillou, J. Wang, A. Steele, S.B. Shirey: *Science*, **334**, 54 (2011).
- [14] M. Satish-Kumar, H. So, T. Yoshino, M. Kato, Y. Hiroi: *Earth. Planet. Sci. Lett.*, **310**, 340 (2011).
- [15] J. Horita, V.B. Polyakov: *Proc. National Acad. Sci.*, **112**, 31 (2015).
- [16] M.M. Grady, I.P. Wright, C.T. Pillinger: *Meteorit. Planet. Sci.*, **32**, 863 (1997).
- [17] M.M. Grady, A.B. Verchovsky, I.P. Wright: *Int. J. Astrobiol.*, **3**, 117 (2004).
- [18] M.M. Grady, I.P. Wright: *Space Sci. Rev.*, **106**, 231 (2003).
- [19] Y. Bottinga: *Earth Planet. Sci. Lett.*, **5**, 301 (1969).
- [20] Y. Nakajima, E. Takahashi, S. Toshihiro K. Funakoshi: *Phy. Earth Planet. Int.*, **174**, 202 (2009).
- [21] O.T. Lord, M.J. Walter, R. Dasgupta, D. Walker, S.M. Clark: *Earth Planet. Sci. Lett.*, **284**, 157 (2009).
- [22] V.N. Reutsky, Y.M. Borzdov, Y.N. Palyanov: *Diamond Relat. Mater.*, **21**, 7 (2012).
- [23] Y.N. Palyanov, Y.V. Bataleva, A.G. Sokol, Y.M. Borzdov, I.N. Kupriyanov, V.N. Reutsky, N.V. Sobolev: *Proc. Natl. Acad. Sci.*, **110**, 20408 (2013).
- [24] V.N. Reutsky, Yu.N. Palyanov, Yu.M. Borzdov, A.G. Sokol: *Russian Geol. Geophys.*, **56**, 239 (2015).
- [25] V.N. Reutsky, Yu.M. Borzdov, Yu.N. Palyanov: *Chem. Geol.*, **406**, 18 (2015).
- [26] P. Deines, F.E. Wickman: *Geochim. Cosmochim. Acta*, **39**, 547 (1975).
- [27] R. Brett: *Geochim. Cosmochim. Acta*, **31**, 143 (1967).
- [28] E. A. Schauble: *Eos Trans AGU* 90(52), Fall Meet Suppl, # V11C-1967, (2009).
- [29] D.J. Stevenson: *Nature*, **451**, 261 (2008).
- [30] F. Albarede: *Nature*, **461**, 1227 (2009).
- [31] J. Zachos, M. Pagani, L. Sloan, E. Thomas, K. Billups: *Science*, **292**, 686 (2001).
- [32] V. Polyakov: *Science*, **323**, 912 (2009).
- [33] A. Shahar, V.J. Hillgren, E.D. Young, Y. Fei, C.A. Macris, L. Deng: *Geochim. Cosmochim. Acta*, **75**, 7688 (2011).
- [34] R.C. Hin, C. Fitoussi, M.W. Schmidt, B. Bourdon: *Earth Planet. Sci. Lett.*, **387**, 55 (2014).
- [35] A. Shahar, V.J. Hillgren, M.F. Horan, J. Mesa-Garcia, L.A. Kaufman, T.D. Mock: *Geochim. Cosmochim. Acta*, **150**, 253 (2015).
- [36] A. Shahar, E.A. Schauble, R. Caracas, A.E. Gleason, M.M. Reagan, Y. Xiao, J. Shu, W. Mao: *Science*, **352**, 580 (2016).

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